Thermal irreversibility demystified.

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Abstract:

Purpose: To understand the difference between irreversibility in heat and work transfer processes. To explain that Helmholtz or Gibbs energy does not represent 'free' energy but is a measure of loss of Carnot (reversible) work opportunity.

Approach: The entropy of mass is described as the net temperature-standardised heat transfer to mass under ideal conditions measured from a datum value. An expression for the 'irreversibility', is derived in terms of work loss (W_{loss}) in a work transfer process, unaccounted heat dissipation (Q_{loss}) in a heat transfer process and loss of net Carnot work (CW_{net}) opportunity resulting from spontaneous heat transfer across a finite temperature difference during the process. The thermal irreversibility is attributed to not exploiting the capability for extracting work by interposing a combination of Carnot engine(s) and/or Carnot heat pump(s) that exchanges heat with the surrounding and operates across the finite temperature difference.

Findings: It is shown, with an example, how the contribution of thermal irreversibility, in estimating reversible input work, amounts to a loss of an opportunity to generate net work output. The opportunity is created by exchanging heat with surroundings whilst transferring the same amount of heat across finite temperature difference. An entropy change is determined with a numerical simulation including calculation of local entropy generation values and results are compared with estimates based on an analytical expression.

Originality: A new interpretation of entropy combined with an enhanced mental image of a combination of Carnot engine(s) and/or Carnot heat pump(s) is used to quantify thermal irreversibility.

Keywords: Entropy; Entransy; Exergy Destruction; Entropy Generation; The Second Law of Thermodynamics; Irreversibility.

Paper Type: Conceptual Paper

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Nomenclature:

CW_{net}: The net Carnot (reversible) work opportunity created by interposing a combination of Carnot engine(s) and/or Carnot heat pump(s) that exchanges heat with the surrounding and operates across the finite temperature difference. The loss of CW_{net} opportunity is defined as the thermal irreversibility.

du: An infinitesimal change in the specific internal energy (J/kg) of a control volume.

U: The internal energy of control volume (J).

δQ: An infinitesimal amount of heat transfer to the control volume.

δQ_{gain}: An infinitesimal value of the heat gain due to work loss (W_{loss}) is assumed to have appeared under ideal conditions.

Q_{loss}: An unaccounted heat dissipation to surroundings during a heat transfer process.

δW: An infinitesimal amount of work transfer to the control volume.

G: Gibbs energy.

F: Helmholtz energy.

H: The enthalpy of fluid under consideration.

I: Irreversibility – the sum of the loss of work, W_{loss}, in a work transfer process, unaccounted heat dissipation to immediate surrounding, Q_{loss}, in a heat transfer process and the thermal irreversibility or the loss of work opportunity, CW_{net}, when heat is transferred across finite temperature difference.

q: Heat flux across the control volume boundary.

S: The entropy of mass within a control volume (J/K). It is defined as the net temperature-standardised heat transfer to mass under ideal conditions measured from a datum. It is a measure of the heat transfer the mass has experienced under ideal conditions.

$\bar{\dot{S}}$: Volume averaged entropy rate within the control volume (W/ m^3 K).

$\dot{S}_{local}$: Nodal entropy rate values in determined in a finite element simulation (W/K).

$\Delta S_{c.v.}$: Change in the entropy of the control volume (J/K).

S_{final}: Final entropy of the control volume (J/K).

$S_{initial}$: Initial entropy of the control volume (J/K).

S_{in}: Entropy of mass transferred to the control volume (J/K).

S_{out}: Entropy of mass transferred from the control volume (J/K).

S_{gen}: Entropy generation term. It is a measure of <u>generation</u> of temperature standardised irreversibility.

S^*: The dimensionless entropy generation term of the fluid.

$\dot{S}_{cond}$: Local entropy generation rate due to conduction.

$\dot{S}_{conv}$: Local entropy generation rate due to viscous dissipation.

T: Temperature (K) of a control volume under uniform conditions.

$\bar{T}$: Volume averaged temperature within the control volume in K.

T_{local}: Nodal temperature values in the finite element simulation.

T_{mass}: Temperature (K) of a control volume under uniform conditions.

T_H: The temperature of a source with which the control volume has exchanged heat with.

T_L: The temperature of a sink with which the control volume has exchanged heat with.

T_0: The atmospheric (constant) temperature in Kelvin (K)

$\bar{T}_b$: Volume averaged boundary temperature at the heating section.

V_{local}: Nodal volume values in the finite element simulation.

W_{loss}: Work loss (energy dissipated as heat) in a work transfer process due to irreversibility.

Z_{diss}: Entransy dissipation term.

1. Introduction

The thermal irreversibility topic has gained much attention since Guo et al. (2007) presented an analogy between heating a piece of solid (metal) and charging an electric capacitor. It is claimed that the entransy concept was developed to fill an existing gap in the heat transfer analysis that there was no measure of irreversibility that was directly related to the optimization of heat transfer not involving in a thermodynamic cycle or heat-to-work conversion (Guo et al. 2014). The differential change in entransy for an incompressible object is given by (*du T*) whereas (*du/T*) that represents a differential change in entropy. According to Guo (2014 a), the entransy of a system represents its heat transfer ability during a time period without heat-work conversion and consequently is a function of the temperature only, while the entropy of a system, which can measure the system ability of heat-work conversion, is a function of two independent system properties. Guo classifies heat transfer processes into two categories according to their purpose (Guo 2014 a, Chen et al. 2013): for heat-work conversion in thermodynamic cycles and for pure object heating or cooling, and recommends to use the entropy generation rate as the measure of the heat transfer (thermal) irreversibility for the first category. For the second category Guo proposes to use the entransy dissipation rate as the measure of the thermal irreversibility.

Cheng and Liang (2019) have attempted to reinforce the credibility of the analogy between the heat and electrical conduction even though the irreversibility, or the loss of work, referred to as Joule heating (I²R losses) are physical energy losses resulting from a work transfer process. This analogy is incorrect and must not be used. The mechanisms for irreversibility during heat transfer and work transfer process are distinctively different. It is true that the energy dissipation due to irreversibility in a work transfer process always occurs in the form of heat and hence its effect appears in both the first and second law of thermodynamics.

The effect of thermal irreversibility, or the irreversibility in a heat transfer process when heat flows across a finite temperature difference, can only be accounted by the second law of thermodynamics. This paper defines thermal irreversibility as a loss of the net Carnot (reversible) work opportunity. The effect of thermal irreversibility does not appear in the first law of thermodynamics, or the conservation of energy principle, as it represents a loss of work opportunity rather than loss of work.

Bejan has undoubtedly pioneered the research on quantifying irreversibility in heat and flow problems since seventies and has been one of the main advocates of using the minimisation of the entropy generation principle (Bejan 1977, 1978, 1979, 1982, 1987). The mathematical equations proposed are rigourous and widely accepted. Using the TdS relationships and the second law of thermodynamics expression, Bejan categorised the work lost due to irreversibility in heat and fluid flows into two parts: the first part is the energy lost due to fluid friction (viscous effect) and the second part is the energy loss due to thermal irreversibility. In addition to thermal and fluid friction irreversibility, Qayyum et al. (2019) used terms associated with Joule dissipation and diffusive irreversibility. Armaghani et al. (2019) used non-dimensional form of entropy generation term to model the effect of heat source location on heat transfer. Sheremet et al. (2017) used the Bejan number to compare the effect of fluid friction and heat transfer irreversibility on the natural convection of nanfluid flow in a wavy cavity. Several authors (Ellahi et al. (2020), Riaz et al. (2021), Akbarzadeh et al. (2018) and Sheikholeslami et al. (2019)) have studied the effect of magnetic and electromagnetic field parameter as well as radiation parameter on irreversibility for flow of nano-fluids through porous media. Authors non-dimensionalised the entropy generation term with a characteristic entropy generation rate. Lukose and Basak (2021) used the heat transfer and fluid friction contributions of the entropy generation term to study the effect of container curved and straight walled shapes on thermal performance or efficiency of convection process. At low Reynolds number (~1000) the effect of thermal irreversibility was dominant in comparison to fluid friction irreversibility. It is relatively easy to visualise how fluid flow losses can be reduced by minimising fluid friction irreversibility. Identifying methods to minimise the thermal irreversibility component of the entropy generation term is more challenging particularly when the heat flows across a finite temperature difference without any work conversion (simple heating or cooling process).

Subject to the following condition, $\Delta T << T$ i.e. $(1 + \frac{\Delta T}{T}) \approx 1$, the entropy generation rate for the thermal irreversibility part is shown equal to $\frac{k(\nabla T)^2}{T^2}$. Bejan (1978) derived an expression for the dimensionless entropy generation rate, $\frac{S_{gen} T}{q}$, as follows:

$$\frac{S_{gen} T}{q} = \left(\frac{\Delta T}{T}\right)\left(1 + \frac{\Delta T}{T}\right)^{-1} \tag{1}$$

This expression holds irrespective whether the condition $\Delta T << T$ is satisfied or not. T is the absolute temperature value of mass in a control volume at a given spatial location and temporal instance. Hesselgreaves (2000) reviewed various approaches to second law analysis of one dimensional heat transfer problems including the approach given by Bejan (1978) and Witte and Shamsundar (1983).

Liu et al. (2011) expressed the entropy generation rate, $\frac{k(\nabla T)^2}{T^2}$, as a dot product of temperature-standardised heat flux term, $\frac{q}{T}$, and $-\frac{\nabla T}{T}$. The entransy dissipation term, $k(\nabla T)^2$, is expressed as a dot product of qT and $-\frac{\nabla T}{T}$. This dot product cancelled the temperature value that represented the temperature level and simplified the entransy dissipation minimisation problem as minimisation of the square of temperature gradients. The results were shown different to the ones obtained from the traditionally used entropy generation minimisation method and has been claimed as more appropriate for optimization of the heat transfer process (Liu et al. 2011, Chen et al. 2011).

Whether the cancellation of the temperature value that represents the temperature level at which the heat transfer has occurred from degrades or enriches information content of thermal irreversibility is explored in this paper.

Since the introduction of entransy in 2007, the Clarivate Web of Science citation report identified 566 publications with the word 'entransy' and it is cited 12,131 times producing an H-index of 52 as of 31st December 2021 (Figure 1). These numbers illustrate the scale of intense academic engagement and scrutiny that the entransy concept has received over the last decade.
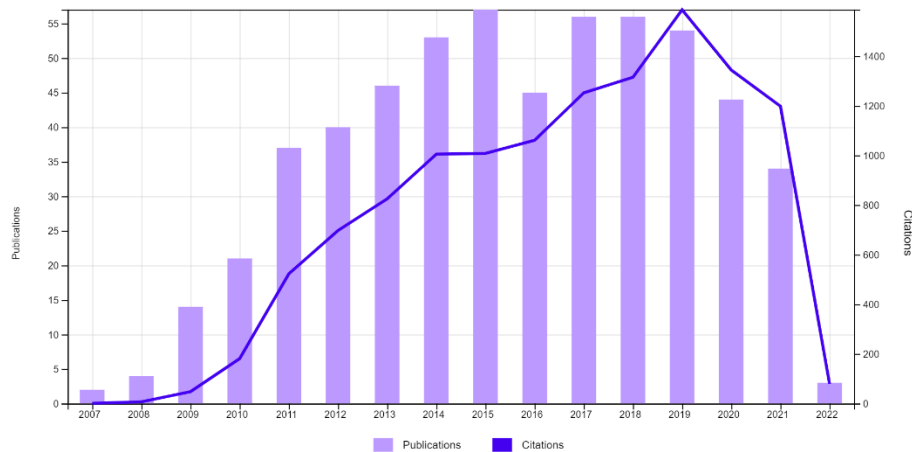
Figure 1: The Clarivate Web of Science citation report for 'entransy' as of 31st December 2021. Average citations per year are in excess of 800.

Bejan (2014, 2018) is a vocal critic of using the entransy minimisation principle and has claimed the entransy research as duplication of science by introducing new terms suggesting an impression of citations cartel and nationalism. Recently, he has argued that all of the entransy papers are worthless (Bejan 2020). Oliveria and Milanez (2014) showed the equivalence between the entransy dissipation and entropy generation terms.

The relevance of entransy in quantifying the thermal irreversibility is explained by Chen, Guo and Liang (2014) in one their rebuttals and is reproduced below in their own words:

"Irreversibility is indeed a universal tendency in nature, but entropy generation and exergy destruction are not the only measures of the irreversibility of any heat transfer process. When the transferred heat is used for doing work, the entropy generation is the irreversibility measure and the entropy generation minimum is the heat transfer optimization objective to maximize heat-work conversion efficiency. Oppositely, when the transferred heat is used to only warm or cool an object, the entransy dissipation is the irreversibility measure and the entransy dissipation extreme is the optimization objective to maximize heat transfer coefficient. Please take the sentence as a whole and do not separate it into two parts. For instance, for heat conduction problems with heat flux boundary conditions, the objective of entropy generation minimization is to minimize the average difference of the reciprocal of the temperature, min ($\Delta(1/T)_{ave}$), while that of the entransy extremum principle is to minimize the average temperature difference, min (ΔT_{ave})."

Kostic (2017) reviewed all criticisms, and the subsequent rebuttals, surrounding entransy and has cautioned against its subjective praise or criticism. He has pointed out that currently there is no justification on why the product (*du T*) is a better or worse term in comparison to the division (*du/T*). As both terms represent the quantity and quality of heat, i.e. the stored thermal heat and its temperature level, he has envisioned that entransy may contribute to better comprehension of the often obscured and elusive thermal phenomena of thermal irreversibility.

Guo (2014 b) has made the following two observations/concerns in his rebuttal to Bejan (2014). These concerns have not yet been responded to in the open literature.

"1. For pure heat transfer processes not concerning heat to work conversion, neither ambient nor absolute temperature should be <u>blindly</u> added into the irreversibility measure and the corresponding optimization objective.

2. The entransy approach is valid for various heat transfer process not involved in a thermodynamic cycle without the limitation of $\Delta T \ll T$, whereas the entropy or exergy approach is not. <u>Why not to discuss the case that $\Delta T \ll T$ is not held.</u>"

It is also important to understand how authors researching the entransy concept perceive its interpretation. In a recent paper Liu et al. (2021) have explained the physical interpretation of entransy as follows: "*The scientific problem behind these arguments is: whether entransy and entropy are equivalent physical concepts or whether entransy dissipation and entropy production have an equal effect. It is clear that entransy can correspond to the energy in other transport systems, such as kinetic energy, potential energy, electrical energy and so on. Therefore, physical meaning of the entransy can only be equivalent to the energy but not to entropy.*". The authors go further and claim that "*(the entransy dissipation rate) … are limited to the framework related to the first law of thermodynamics, not to the second law of thermodynamics*". It is not clear whether this claim was noticed and assessed by the referees during the peer review process of the International Journal of Heat and Mass Transfer. It is commonly understood that work transfer irreversibility terms do contribute to the first law of thermodynamics expression. However, it is explained in this paper why any measure of thermal irreversibility can only be accounted in the second law of thermodynamics and NEVER in the first law of thermodynamics. The entropy balance equation based on the second law of thermodynamics accounts for both work transfer and thermal irreversibility terms.

In summary, it appears that the following four claims are emerging from this discussion:

1. Whether the physics associated with heat transfer across a finite temperature difference depends on its purpose in order to require purpose specific approach e.g. whether heat is transferred to:
   (i)   heat or cool an object
   (ii)   achieve heat-to-work conversion.

2. It is claimed that for heat transfer problems that do not relate to heat-to-work conversion, the use of entransy i.e. multiplication of the change in the internal energy du for an incompressible object by the absolute instantaneous temperature T is a better option for minimising thermal irreversibility as compared to entropy that involves a division operation with T.
3. The absolute temperature term is added to the thermal irreversibility measure without justification.
4. The current equations and science does not have an expression for the irreversibility measure when the condition $\Delta T \ll T$ is not satisfied. The entransy dissipation term does not have this limitation.

The aim of this paper is to unravel the elusiveness of thermal irreversibility by identifying a unique measure that only entropy determines and to provide the much needed justification to the claim whether entransy is more suitable than entropy to quantify thermal irreversibility when heat is transferred to heat or cool an object.

The objective of this paper is to directly address both of the concerns Guo (2014 b) has made in his rebuttal to Bejan (2014). The objectives are listed below.

1. Refine the entropy concept to develop a unique measure in addition to the existing measure of thermal disorder.
2. Develop a mental image of thermal irreversibility to visualise if the heat transfer across a finite temperature difference can depend on its purpose.
3. Derive an expression for the thermal irreversibility from first principles to assess whether it is necessary to add the absolute temperature variable in the irreversibility measure for the following two cases:
   a. $\Delta T \ll T$ condition is satisfied.
   b. $\Delta T \ll T$ condition is not satisfied

Section 2 briefly reviews some of the current interpretations of entropy used in the literature and introduces a mental image for visualising thermal irreversibility. Section 3 defines entropy, explains

ideal conditions and describes the associated temperature-standardisation concept. This interpretation has allowed the change in the entropy values under real and ideal conditions to be equated with each other for a control volume with, or without, mass transfer. This led to the development of a new expression for calculating the entropy generation term in terms of the loss of net Carnot work, CW_{net}, opportunity during heat transfer across a finite temperature difference in a process, unaccounted heat dissipation, Q_{loss}, to immediate surrounding in a heat transfer process and the work loss, W_{loss}, that occurred during work transfer in the process. It is shown how the Gibbs and Helmholtz energy is related to the net Carnot work, CW_{net}, opportunity. An example is illustrated in Section 4 to discuss how the proposed methodology is applied and how thermal irreversibility can be used as a tool to gain insights on developing novel energy efficient solutions. Section 5 derives an expression for thermal irreversibility for simple heat conduction achieving heating or cooling effect using the Carnot heat engine and heat pump analogy. Section 6 presents a numerical example for a transient process with heat generation and natural convection to relate the local entropy generation term with the total entropy generation between the final and initial states. The paper is concluded in Section 7.

2. Entropy, disorder and irreversibility

Perhaps, one of the main reason why the thermal landscape is elusive is because entropy has been _exclusively_ associated with thermal disorder of molecules and how organized/disorganized energy is (Kostic 2014). It is often forgotten that entropy is not the only measure of thermal disorder. Other properties such as 'enthalpy' and/or 'temperature' of mass are also a measure of thermal disorder.

Entropy is neither elusive nor confusing. We, as a society, are responsible for keeping entropy elusive and confusing. Wilhelm (2021, Chapter 1, p.11) has concluded in his recent book, published by the Royal Society of Chemistry, in the UK, that Classical thermodynamics does not provide an explicit definition of the total entropy. The reality is that the connection of 'entropy and disorder' is engraved at the subconscious level in the young and unsuspecting minds not just by Wikipedia, text books and literature (Bejan 2020) but more importantly, the exam boards. Most of us were introduced with the entropy concept, alongside of the Gibbs energy, while learning chemistry in the final year of school before starting a formal University education. Many chemistry text books define Gibbs energy (G) for an isothermal and isobaric non-flow chemical process as ($H - T_0S$) where H is the enthalpy of fluid under consideration, T_0 is the atmospheric (constant) temperature in Kelvin (K), and S is the entropy of the fluid.

Many international exam boards, including some of the UK's leading exam boards, such as Oxford Cambridge and RSA (OCR) [I], the Assessment and Qualification Alliance (AQA) [II], the Welsh Joint Education Committee (WJEC) [III] and a qualification brand, 'Edexcel' for academic and general qualifications from Pearson [IV], still use the term 'Gibbs _free_ energy' rather than 'Gibbs energy' whilst introducing the concept, probably for the first time, to students studying chemistry at A levels. As an example, the Edexcel board explains the Gibbs free energy "as the enthalpy content minus TS which represents the substance's energy that is already disordered. This difference is the energy that is available to become disordered by doing work" [IV]. Entropy is defined as "a measure of the dispersal of energy in a system, which is greater, the more disordered a system" by the OCR board [I]. The AQA board introduces entropy as a concept of increasing disorder [II], which is echoed by the Edexcel board that defines entropy as a measure of disorder [IV]. The WJEC board defines entropy of a system as "a measure of the freedom possessed by particles within it and the increase in entropy towards a maximum for all natural changes" in it's A Level chemistry specification [III]. This makes it very difficult for everyone to unlearn the mental image of disorder and chaos from entropy.

Order and disorder are a distinct phenomenon to irreversibility. Bejan (2020) has argued that 'increasing disorder' is a misunderstanding of entropy. He has associated generation of irreversibility

with an entropy generation term and introduced entropy change (not "entropy") as "*a mathematical expression formulated by Clausius in order to show the irreversibility of "any" process (any change of state) experienced by any system. This way, the second law is an inequality. The measurement of the severity of the inequality sign is the entropy generated during the process, and this is being used as a measure of how irreversible (dissipative, imperfect) the process is*". Associating entropy with order/disorder or organized/disorgaised energy is a pointless exercise. Its connection to the probability of energy states as perceived in statistical thermodynamics narrows down its applicability. In Bejan's (2020) words: "*thermodynamics is immensely more general and more applicable than statistical mechanics*".

Lambert's (2002 a) view of entropy as a measure of energy dispersal at temperature T is a significant advancement over an incorrect interpretation of entropy; a measure of molecular disorder. The description of entropy; as a measure of the freedom possessed by particles within it, needs to be avoided, including any references to statistical micro-states, as it is likely to cause confusion in understanding the entropy concept in the context of Classical thermodynamics. Lambert's (2002 a) energy based view of entropy is certainly a step in the right direction. However, the interpretation of energy diffusion, or dispersal, to more microstates does not give clarity on how heat transfer affects the internal energy, flow work, boundary work or kinetic energy of mass of a control volume at the continuum level. It does not account for heat dissipation due to irreversibility in a work transfer process. Indeed, the last sentence in Lambert's (2002 b) second paper refers to entropy change as being related to the dissipation of energy, however, it was used in the context of dispersal of molecular energy. A distinction is made in this paper to relate entropy change from the dispersal of energy to temperature-standardised heat transfer across the control volume boundary, including heat dissipation resulting from work loss due to an irreversibility in a work transfer process.

Ben-Naim's (2011) work on Shannon's measure of information offers a statistical based explanation of entropy. The mixing processes described in the first figure of Ben-Naim's paper illustrates an example of why Shannon's measure of information interpretation of entropy is useful as compared to the energy based interpretation of Lambert. The mixing process of two ideal gases follow a reversible isothermal expansion process. It is obvious that the internal energy for the ideal gas does not change as the temperature remains constant. The changes in volume are described as boundary work. However, what is not mentioned in the paper is that, although the pressure will remain directly proportional to the density of the gas under reversible isothermal conditions, the boundary work is either supplied externally by an infinitesimal addition of heat to the gas, or another frictionless mechanical device. This is the only way that the internal energy and the temperature of the control volume can remain constant. The change in the entropy of the control volume resulting from volume changes is equal to the corresponding changes to heat transfer for reversible isothermal processes. However, it is not clear how Shannon's measure of information would explain heat dissipation due an irreversibility that is associated with all real processes.

Bhattacharyya and Dawlaty (2019) have attempted to relate statistical interpretation of entropy with thermodynamic entropy. This connection seems unnecessary if the objective of the study is to understand thermodynamic efficiency, the existence of impossible states or processes, or to quantify and minimise irreversibility effects in a process.

2.1 A mental image of thermal irreversibility in terms of loss of Carnot work

Kostic (2020) explains that 'entropy is always generated with heat generation due to all kinds of irreversibilities, including the conduction heat transfer'. In one of the early papers, Kostic (2004) used a combined Carnot heat engine-heat pump analogy to explain reversible heat transfer. The Carnot heat engine drove the heat pump and the heat rejected by the engine was fed to the heat pump. This allowed the heat transfer to occur without loss of Carnot work opportunity or the thermal irreversibility. Bejan (2019) has also used Carnot engine analogy to explain reversible and irreversible heat transfer. However, one of the best analogy that is often not cited is the analogy of a combined Carnot heat engine-heat pump given by Witte and Shamsundar (1983). The analogy was given for a heat exchanger but is

equally applicable to general heat transfer problems across a finite temperature difference (Figure 2). The mental image of Witte and Shamsundar's Carnot heat engine-heat pump analogy is extended to all four combinations as heat is transferred from $T + \Delta T$ to T (Figure 3 a: $T > T_0$, b: $T + \Delta T < T_0$) and from T to $T + \Delta T$ (Figure 3 c : $T > T_0$, d: $T + \Delta T < T_0$). When heat is transferred from a high temperature to low temperature for heating purpose (Figure 3 (a, b)), the net Carnot work output value that represents thermal irreversibility is notional, it represents an opportunity. For cooling purpose, the heat is transferred from a lower temperature to higher temperature and the net Carnot work input value is real or physical (Figure 3 (c, d)). It needs to be made clear here that the term 'Carnot work' is used in this paper as a general case to cover all 'reversible work'.
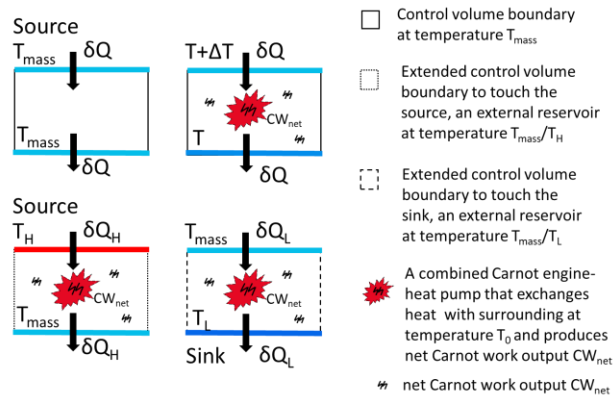

Figure 2: When heat is transferred from a high temperature to low temperature for a purpose of heating, the net Carnot work output value that represents thermal irreversibility is a notional value. It represents an opportunity to produce work.
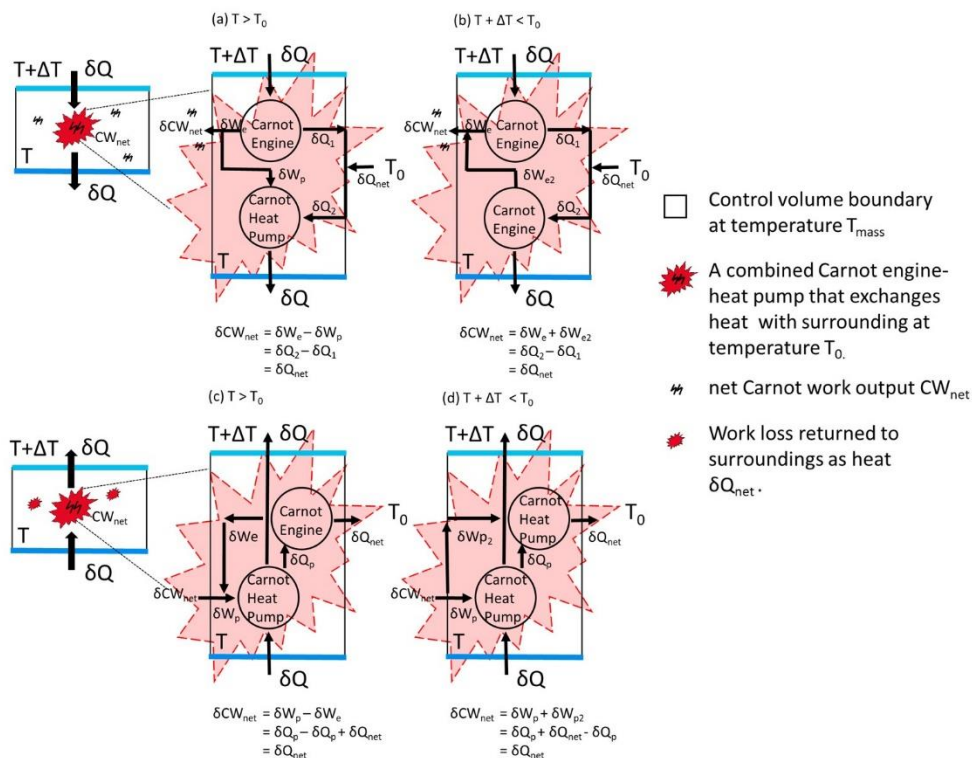

Figure 3: A mental image of thermal irreversibility based on Witte and Shamsundar (1983). Heat is transferred from $T + \Delta T$ to T (a) $T > T_0$, (b) $T + \Delta T < T_0$ and from T to $T + \Delta T$ (c) $T > T_0$, (d) $T + \Delta T < T_0$).

3. The entropy of mass within a control volume

A new description that excludes words 'disorder' and 'disorganised', helps to create a mental image of entropy is proposed in this paper. The entropy is described as a 'measure of the heat transfer the mass has experienced under ideal conditions'.

Entropy is a property of the mass i.e. mass at a given state will have a unique entropy value irrespective of how the state was reached. The entropy of mass is described as the net temperature-standardised heat transfer to mass under ideal conditions measured from a datum.

There are three important concepts to note in this description:

  (i)   temperature standardisation

  (ii)   ideal conditions

  (iii) a datum

The ideal conditions for heat transfer are described in the next sub-section. The entropy value is assumed as zero at an arbitrary chosen datum. This is the reason why an estimation of an entropy value at a given state is different in many thermodynamics tables, or diagrams such as enthalpy-entropy or pressure-entropy.

It is important to understand the temperature value used for standardisation for both real and ideal cases. Clausius (1879) (p 90) defined that in a reversible cyclical process, every element of heat taken in, positive or negative, should be divided by the absolute temperature at which it is taken in, and the newly formed differential be integrated for the whole course of the process. Here, the integral is observed as zero. Clausius has suggested to use the magnitude of heat exchanged with the external reservoir and that it be standardised with the reservoir temperature value. It is the temperature of the source (T_H)/sink (T_L)/surroundings (T_0) i.e. the external reservoir temperatures with which the mass has exchanged heat.

In short, you never standardise the heat transfer value with reference to the temperature of mass in a control volume, except under the following two conditions:
  (i)   when the heat is transferred under ideal conditions, as the temperature of the external reservoir remains the same as the temperature of mass in a control volume at all times
  (ii)   when the heat is generated by a source within the control volume rather than being transferred to the mass across the control volume boundary. For example, this happens during an adiabatic irreversible work transfer process. The work loss due to irreversibility reappears as heat gain within the control volume like a heat source. Therefore, to calculate the entropy increase in this case, the infinitesimal value of the heat gain, δQ_{gain}, is assumed to have appeared under ideal conditions, and therefore, it is standardised by the temperature of mass (or control volume).

3.1. Heat transfer under Ideal and Real Conditions and Loss of Carnot Work opportunity

Ideal conditions assume that there is no irreversibility in the process. This is a theoretical possibility that constitutes the most efficient form of heat transfer without any loss of the Carnot (reversible) work opportunity. The heat transferred under ideal conditions assumes the heat transfer to have occurred extremely slowly under quasi-equilibrium conditions. As the mass changes its temperature, T_{mass}, with heat transfer (Figure 4a and 5a), it is assumed that at all times the mass remains in thermal equilibrium with the external reservoir with which it exchanged heat. The entropy change value, ΔS, under ideal conditions is standardised with the mass temperature, T_{mass}. The isothermal heat transfer process at each quasi-equilibrium state constraints the Carnot heat engine work output equal to the Carnot heat

pump work input. The heat rejected by the Carnot engine is input to the heat pump. The net Carnot work, δCW_{net}, is zero at each quasi-equilibrium state. This integration gives a summation of all temperature-standardised heat transfer values δQ_H, or δQ_L, under ideal conditions. The equation is $S = S_0 + \int \delta Q / T_{mass}$, where S_0 is an arbitrary chosen datum value taken as the initial value and assumed as zero.

The ideal-conditions assumption helps us to relate the magnitude of heat exchanged with the external reservoir with the control volume properties. Therefore, it is this assumption that makes it possible for entropy to be defined as a property of mass. As a result, the change in the entropy of mass can be interpreted as a measure of the heat transfer the mass has experienced under ideal conditions.
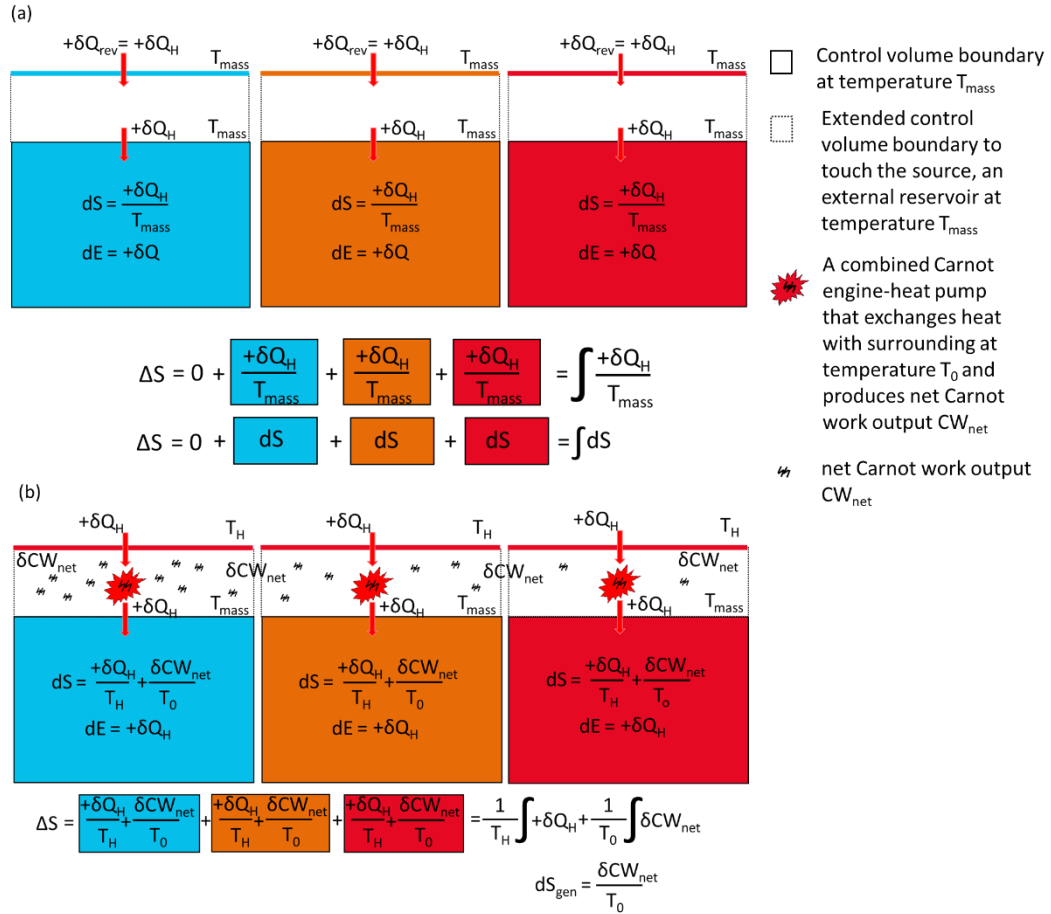

Figure 4. Heat transfer to control volume under **(a)** ideal and **(b)** real conditions. The ΔS value calculated for the corresponding reversible $+\delta Q_{rev}$ case is same as for the real $+\delta Q$ case.

In reality, the heat transfer occurs at the fastest possible rate under given constraints. This contrasts the quasi-equilibrium assumption. For a real process, if we assumed that the control volume exchanges heat Q_H with a source at constant temperature T_H, and/or rejects heat Q_L to a sink at constant temperature T_L, then the resulting loss of net Carnot work, δCW_{net}, output is determined with the summation of the following two expressions:

(a) The difference between the work output of a Carnot engine that receives heat δQ_H at temperature T_H, which operates between temperatures T_H and T_0, and the work input to a Carnot heat hump that delivers heat δQ_H at temperature, T_{mass}, which operates between temperatures T_{mass} and T_0 (Figure 4b).

(b) The difference between the work output of a Carnot engine that receives heat δQ_L at temperature, T_{mass}, and operates between temperatures T_{mass} and T_0, and the work input to a

Carnot heat hump that delivers heat δQ_L at temperature T_L which operates between temperatures T_L and T_0 (Figure 5b).
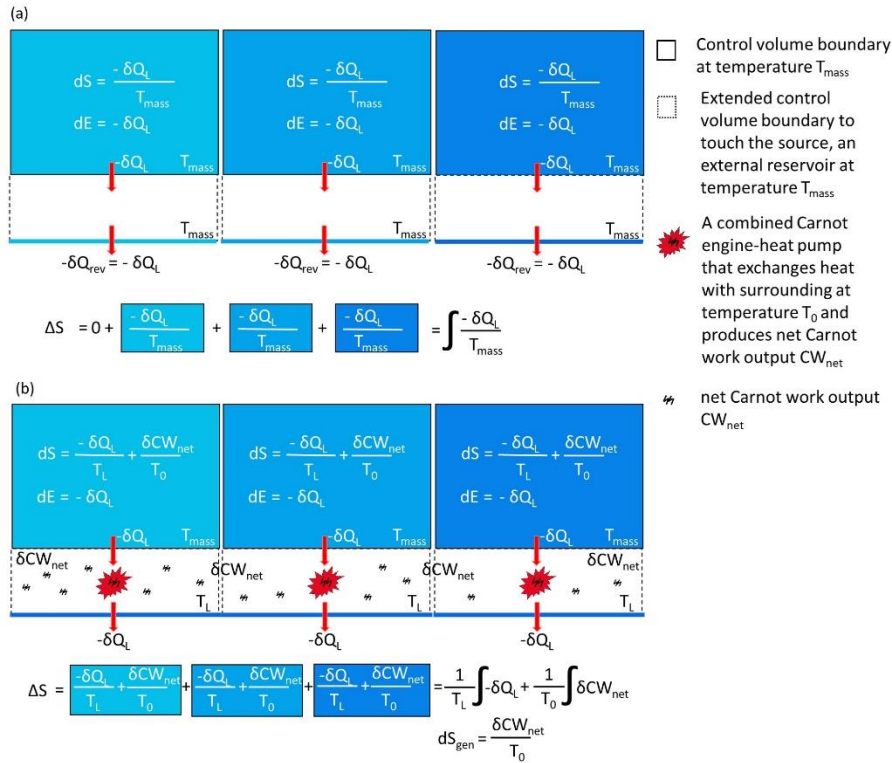

Figure 5. Heat transfer from control volume mass under **(a)** ideal and **(b)** real conditions. The ΔS value calculated for the corresponding reversible $-\delta Q_{rev}$ case is same as for the real $-\delta Q_L$ case.

This loss of net Carnot work output, CW_{net}, is captured within the extended boundary (Figures 4b and 5b). To calculate the resulting entropy change ΔS value of control volume mass; $+\delta Q_H$ is standardised with the source temperature, $-\delta Q_L$ is standardised with the sink temperature, and δCW_{net} with the surroundings (atmospheric) temperature value. The summation is done until the control volume reaches the final temperature. The change in the entropy of the control volume for heat addition under real conditions is $+Q_H/T_H + CW_{net}/T_0$, whereas for heat rejection under real conditions, it is $-Q_L/T_L + CW_{net}/T_0$.

3.2 Work transfer, with and without heat transfer, under ideal and real conditions

The ideal conditions during a work transfer process assume no dissipation of energy (Figure 6a (upper half). For a real adiabatic work transfer process, the work loss due to irreversibility, W_{loss}, appears as heat gain, Q_{gain}, within the control volume, and the heat does not cross the control volume boundary (Figure 6a (lower half)).
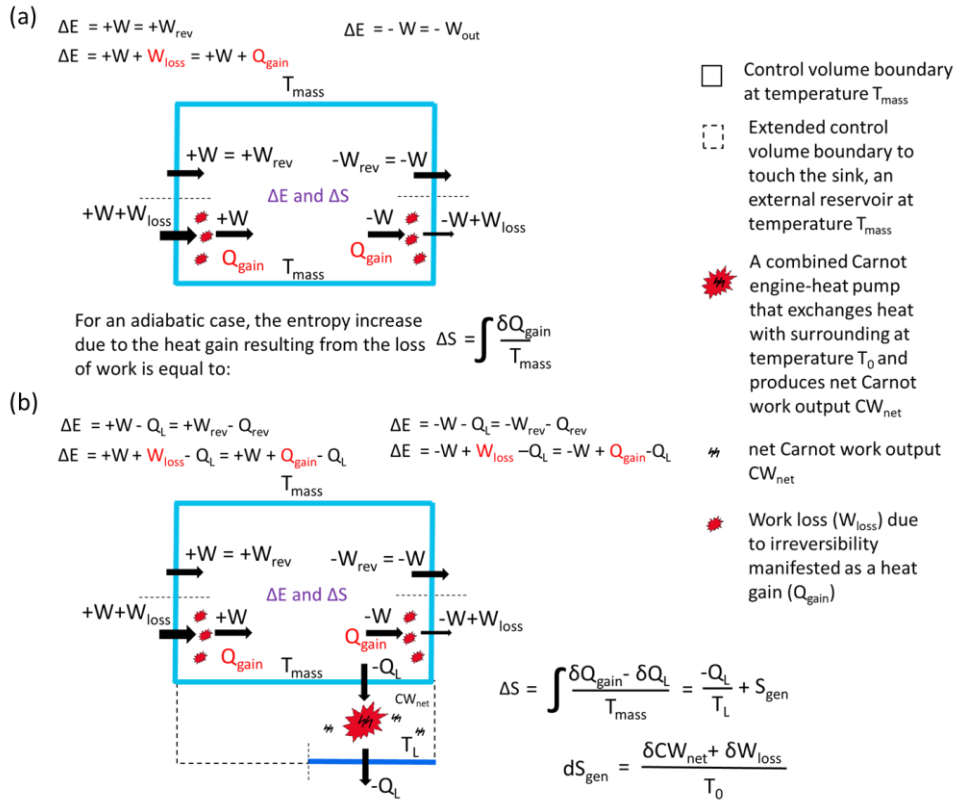
Figure 6. Work transfer to and from control volume: **(a)** without heat transfer under ideal (the upper half of (a)) and real (the lower half of (a)) conditions; **(b)** with heat transfer from the control volume under real (the lower half of (b)) conditions.

The entropy difference is a measure of the heat transfer the mass has experienced under ideal conditions. The entropy of the mass in a control volume changes as the work loss, δW_{loss}, appears as heat gain, δQ_{gain}, within the control volume. This results in increasing the temperature of the mass T_{mass}. Therefore, the term δW_{loss}, or δQ_{gain}, is standardised with T_{mass}. Note that under uniform condition assumption, there is no spatial variation of temperature (T_{mass}) across control volume and the temperature will only depend on time. The increase in the entropy, due to Q_{gain}, is calculated by integrating the ($\delta Q_{gain} / T_{mass}$) term from an initial to a final condition. It contributes to the entropy generation term. There is no heat transfer across the control volume boundary under adiabatic conditions. The heat gain (Q_{gain}) appears within the control volume under ideal conditions. There is no heat transfer across finite temperature difference within the control volume. Therefore, the net Carnot work output (δCW_{net}) during the heat gain process, or the thermal irreversibility, is zero. An example with a numerical simulation is illustrated in Section 6 to further clarify this concept.

For a non-adiabatic work transfer process, the heat transfer across control volume boundary is Q_L (Figure 6b (lower half)). The net heat transfer to the control volume is $Q_{gain} - Q_L$.

The corresponding entropy change is given by the integral of ($\delta Q_{gain} - \delta Q_L$)/$T_{mass}$. The entropy difference under real conditions is given by $-Q_L/T_L + S_{gen}$. This entropy generation term is a measure of irreversibility which is the sum of temperature standardised the loss of work, δW_{loss} or δQ_{gain}, and the loss of net Carnot work, δCW_{net}, opportunity.

For the combined Carnot engine-heat pump, at each quasi-equilibrium step, the Carnot engine operates between temperature values T_{mass} and T_0, and the Carnot heat pump between temperature values T_L and T_0. The resulting entropy generation term is:

$$S_{gen} = (W_{loss} + CW_{net}) / T_0.$$

A heat transfer process under real condition may also be associated with an unaccounted heat dissipation to immediate surrounding. This dissipation is referred to as Q_{loss} and needs to be considered in the entropy generation term. The W_{loss} term is due to the irreversibility in a work transfer process and CW_{net} is corresponds to the thermal irreversibility.

$$S_{gen} = (W_{loss} + CW_{net} + Q_{loss}) / T_0. \tag{2}$$

The irreversibility (I) and the exergy destruction term $(T_0 S_{gen})$ is expressed as:

$$I = T_0 S_{gen} = W_{loss} + CW_{net} + Q_{loss} \tag{3}$$

3.3 An expression for thermal irreversibility during heat exchange with a source and sink.

The change in the entropy of mass is a measure of the heat transfer the mass has experienced under ideal conditions. Note that the heat gain term, δQ_{gain}, although is a result of the loss of work, W_{loss}, during a work transfer process, appears as heat gain within the control volume under ideal heat transfer conditions. A uniform temperature distribution is assumed within a control volume. It is assumed that there is no unaccounted heat dissipation during a heat transfer process ($Q_{loss} = 0$).

The entropy change expression for a process with work transfer under real conditions and heat transfer under ideal conditions (source and sink temperature is equal to T_{mass}) is:

$$\Delta S_{c.v.} = S_{final} - S_{initial} + (S_{out} - S_{in})_{mass\ flow} = \int(\delta Q_H / T_{mass}) - \int(\delta Q_L / T_{mass}) + \int(\delta Q_{gain} / T_{mass}) \tag{4}$$

Where:

$\Delta S_{c.v.}$: Change in the entropy of the control volume (J/K)

S_{final}: Final entropy of the control volume (J/K)

$S_{initial}$: Initial entropy of the control volume (J/K)

S_{in}: Entropy of mass transferred to the control volume (J/K)

S_{out}: Entropy of mass transferred from the control volume (J/K)

The term $\int(\delta Q_{gain} / T_{mass})$ contributes to the entropy generation term and is a measure of work transfer irreversibility, W_{loss}, in the process. The average temperature, $T_{mass,avg}$, is determined from the following equation:

$$\Delta S_{c.v.} = Q_{net} / T_{mass,avg} \tag{5}$$

Equation 4 is expressed as:

$$\Delta S_{c.v.} = (Q_H / T_{mass,avg}) - (Q_L / T_{mass,avg}) + (Q_{gain} / T_{mass,avg})$$

$$T_{mass,avg}\ \Delta S_{c.v.} = Q_H - Q_L + Q_{gain}$$

$$0 = T_{mass,avg} \, \Delta S_{c.v.} - Q_H + Q_L - Q_{gain} \tag{6}$$

If unaccounted heat dissipation to immediate surrounding, Q_{loss}, occurs during a heat transfer process, then the entropy change expression for heat transfer under real conditions is:

$$\Delta S_{c.v.} = (Q_H / T_H) - (Q_L / T_L) + S_{gen}$$

Where, $S_{gen} = (CW_{net} + W_{loss} + Q_{loss}) / T_0$

$$T_0 \, \Delta S_{c.v.} = Q_H \, (T_0 / T_H) - Q_L \, (T_0 / T_L) + T_0 \, S_{gen}$$

$$T_0 \, S_{gen} = T_0 \, \Delta S_{c.v.} - Q_H \, (T_0 / T_H) + Q_L \, (T_0 / T_L) \tag{7}$$

Subtracting Equation 6 from Equation 7, we get:

$$I = T_0 \, S_{gen} = (T_0 - T_{mass,avg}) \, \Delta S_{c.v.} + Q_H \, (1 - T_0 / T_H) - Q_L \, (1 - T_0 / T_L) + Q_{gain}$$

$$I = T_0 \, S_{gen} = (T_0 - T_{mass,avg}) \, \Delta S_{c.v.} + Q_H \, (1 - T_0 / T_H) - Q_L \, (1 - T_0 / T_L) + W_{loss} \tag{8}$$

Using Equation 3:

$$W_{loss} + CW_{net} + Q_{loss} = (T_0 - T_{mass,avg}) \, \Delta S_{c.v.} + Q_H \, (1 - T_0 / T_H) - Q_L \, (1 - T_0 / T_L) + W_{loss}$$

$$CW_{net} + Q_{loss} = (T_0 - T_{mass,avg}) \, \Delta S_{c.v.} + Q_H \, (1 - T_0 / T_H) - Q_L \, (1 - T_0 / T_L) \tag{9}$$

Equation 9 gives an expression for thermal irreversibility when the mass in a control volume has uniform temperature distribution and has exchanged heat with an external source or sink. Note that the Q_{loss} is assumed to be zero in Equation 9.

For Helmholtz (ΔF) and Gibbs energy (ΔG) equations, the temperature is assumed to remain constant at T such that $T = T_0 = T_H = T_L$. For the Gibbs energy equation, $Q_H - Q_L = \Delta H$ where H is the enthalpy of control volume (J) where as for the Helmholtz energy equation, $Q_H - Q_L = \Delta U$ where U is the internal energy of control volume (J). Substituting these values in Equation 7 and multiplying both terms by -1 yields:

$$\Delta F = - T \, S_{gen} = \Delta H - T \, \Delta S_{c.v.}$$

$$\Delta G = - T \, S_{gen} = \Delta H - T \, \Delta S_{c.v.}$$

Using Equation 3 and noting that the W_{loss} term is zero for the Helmholtz and Gibbs energy equation and it is assumed that there is no unaccounted heat dissipation, Q_{loss}, the equation is rewritten as:

$$\Delta F = - CW_{net} = \Delta H - T \, \Delta S_{c.v.}$$

$$\Delta G = - CW_{net} = \Delta H - T \, \Delta S_{c.v.}$$

This, it is shown that the Gibbs, or Helmholtz, energy is NOT free energy as commonly perceived but is equal to the negative of the Carnot (reversible) work opportunity. It should be noted that for non-spontaneous isothermal reactions where ΔG is calculated as a positive number, the entropy balance equation (Equation 7) needs to be applied with an extended boundary assumption to accurately account for the thermal irreversibility yielding a positive entropy generation value.

The expression for thermal irreversibility for heat conduction is derived in Section 5.

4. A numerical example of heating a home on a cold winter night.

Care should be taken in interpreting reversible work input requirement calculated using the entropy generation term that includes contributions from both thermal and work transfer irreversibility. This is explained with an example below.

Assume that a house has lost 500,000 kJ of heat on a cold winter night during a period of ten hours. The house was kept at 22 °C at all times during this period with a controlled heat release from a number of water tanks holding 1000 kg of hot water at 80 °C, and the remaining heat was supplied by an electrical resistance heater. The water was heated to 80 °C with solar energy before the start of the ten-hour period. The outside surrounding temperature during the ten-hour period is 5 °C. The specific heat of water is assumed as 4.18 kJ/kgK. Determine the reversible input work required to heat the house.

4.1 Current approach to a solution:

Assume the house boundary is the control volume, and that the mass does not cross the control volume. The change in the internal energy of air in the house is zero as the temperature of the house remains constant at 22 °C. Hence, using the first law of thermodynamics, the change in the internal energy of water is equal to the heat lost from the house and the heat supplied by the electrical resistance heater (*Win*) i.e.:

$1000\ (kg) * 4.18\ (kJ/kgK) * (22-80)(°C) = -(500,000)\ (kJ) + Win$

$-242,440 = -(500,000) + Win$

$Win = 257,560$ kJ

As the temperature and pressure of air in the house remains constant, the entropy change of air during the ten-hour period is zero. There is no mass flow of air or water across the control volume. The entropy change of water as it cools from 80 °C (353 K) to 22 °C (295 K) is equal to -750.28[2] kJ/K. The outside air temperature is 278 K.

$S_{gen} = -750.28 + (500,000)/278 = 1048.3$ kJ/K

$T_0\,S_{gen} = 278 * 1048.3 = 291,422.3 = 291,422$ kJ

$W_{in,rev} = W_{in} - T_0\,S_{gen} = 257,560 - 291,422 = -33,862$ kJ

Unless, we use Equation 9, it is not clear how thermodynamics insights can be used that can lead to an innovative design of a system that has potential to generate the work output of 33,862 kJ.

4.2 New insights gained with the use of the W_{loss} and CW_{net} terms:

The electrical resistance heater supplied 257,560 kJ of heat. The entropy change of air is zero.

$0 = -257560 / 278 + S_{gen}$
$T_0\,S_{gen} = 257560$ kJ $= W_{loss} + CW_{net} + Q_{loss}$

Each term of Equation 9 that determines CW_{net} is zero. There is no unaccounted heat dissipation to immediate surrounding. Therefore, Q_{loss} is zero. As a result, the term $T_0\,S_{gen}$ is equal to the term W_{loss} which is equal to *257560 kJ.* The net Carnot work for a combined Carnot engine and Carnot heat pump operating between temperature limits 22 °C (295 K) to 5 °C (278 K) is zero as the Carnot efficiency will

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[2] *1000 * 4.18 * ln (295/353) = -750.28.*

be equal to the reciprocal of the Carnot heat pump coefficient of performance. An air sourced Carnot heat pump delivers heat to the house at 22 °C, and is powered by a Carnot engine that takes heat from the house at 22 °C and rejects to the surrounding air at 5 °C. Hence, the reversible work input always remains as zero.

The heat loss from hot water tanks is subdivided into two steps. In the first step the hot water at 80 °C rejects heat into a sink, i.e. house at 22 °C. This heat is lost to surroundings at 5 °C in the second step.

During the first step, as the temperature of water at 80 °C drops to 22 °C under ideal conditions, at each quasi-equilibrium state, a Carnot engine is assumed to have produced an incremental work (δCW). The entropy change of water as it cools from 80 °C (353 K) to 22 °C (295 K) is equal to -750.28 kJ/K.

$$T_0 S_{gen} = 278*(-750.28 + 242440/295) = 19{,}891.18 = 19{,}891 \text{ kJ}. \tag{10}$$
$$= CW_{net} + W_{loss}$$

As W_{loss} is equal to zero during the first step, the work output potential of a Carnot engine that is lost in the first step is 19,891 kJ. The terms in the proposed Equation 8 for the $T_0 S_{gen}$ term give further insights on the Carnot work opportunity.

$$T_0 S_{gen} = (T_0 - T_{mass,avg}) \, \Delta S_{c.v.; \, mass \, flow} - Q_L \, (1 - T_0/T_L)$$

$$19{,}891 = (278 - T_{water,avg}) \, (-750.28) - 242{,}440 \, (1 - 278/295)$$

$$T_{water,avg} = 50.13 \, °C$$

As the heat loss depends linearly on the temperature drop for convective heat transfer, $T_{water,avg}$ is approximately equal to ((80+22)/2) = 51 °C.

The term $Q_H \, (1 - T_0/T_H)$ of Equation 8 is also equal to zero. The term $Q_L \, (1 - T_0/T_L)$ is equal to 13,971.1 kJ and it represents the Carnot work opportunity for the heat that was transferred from the hot water to the house and then eventually rejected from the house to the surroundings. The term $(T_0 - T_{mass,avg})$ $\Delta S_{c.v.; \, mass \, flow}$ is equal to 33,862 kJ and it represents the Carnot work opportunity of a combined Carnot engine-Heat Pump operating between temperatures T_0 and $T_{water,avg}$. A value of 33,862 kJ can also be directly obtained if 278 K (the surrounding temperature value) is substituted in Equation 10 instead of 295K (the temperature of house).

5. An expression for thermal irreversibility during heat conduction.

The expression for the net Carnot work, CW_{net}, opportunity developed in this paper for cases shown in Figure 2 is based on the definition of efficiency, η, given by Witte and Shamsundar (1983) for thermal irreversibility I_T and heat transfer Q.

$$\eta = 1 - \frac{I_T}{Q} = 1 + \frac{T_0}{T_h} - \frac{T_0}{T_c} \tag{11}$$

Bejan (1988) pointed out for very low temperatures, e.g. experienced in cryogenic applications, this efficiency expression leads to a negative number as the thermal irreversibility I_T exceeds the value of heat transferred Q. Hesselgreaves (2000) refers to this as conceptually inconvenient result but has used the concept in his analysis. Figure 3d illustrates why the irreversibility, δI_T which is same as the net Carnot work input δCW_{net}, can exceed δQ at temperatures experienced in cryogenic applications. The δQ_{net} needs to be pumped back all the way to the surrounding temperature T_0. This increases the corresponding value of δCW_{net} and makes it greater than the heat δQ that is being transferred at very low cryogenic operating temperatures.

For heat conduction the terms T_h and T_c are replaced by $T + \Delta T$ to T. The Equation 11 is written as:

$$\frac{\delta CW_{net}}{\delta Q} = -\frac{T_0}{T+\Delta T} + \frac{T_0}{T} \tag{12}$$

A Carnot heat engine operating between temperature $T+ \Delta T$ and T_0 with heat input of δQ will produce Carnot work of $\delta Q\,(1 - T_0/(T+\Delta T))$. A Carnot heat pump, operating between temperature T and T_0 and powered by a Carnot heat engine, takes the necessary heat from the surroundings and delivers δQ at temperature T. The net Carnot work output (δCW_{net}) is given by the following expression which is same as Equation 12:

$$\delta CW_{net} = \delta Q \left(1 - \frac{T_0}{T+\Delta T}\right) - \delta Q \left(1 - \frac{T_0}{T}\right)$$

$$= \delta Q \left(\left(\frac{T - T_0 + \Delta T}{T\left(1+\frac{\Delta T}{T}\right)}\right) - \left(\frac{(T - T_0)\left(1+\frac{\Delta T}{T}\right)}{T\left(1+\frac{\Delta T}{T}\right)}\right)\right)$$

$$= \delta Q \left(\frac{T_0\frac{\Delta T}{T}}{T\left(1+\frac{\Delta T}{T}\right)}\right)$$

$$= \delta Q \, \frac{T_0}{T}\frac{\Delta T}{T}\left(1+\frac{\Delta T}{T}\right)^{-1}$$

Therefore, for a one dimensional heat conduction problem, the local value $\delta CW_{net,}$is expressed in terms of a dimensionless parameter $\frac{T_0}{T}\frac{\Delta T}{T}\left(1+\frac{\Delta T}{T}\right)^{-1}$ that represents quality of heat transfer. For three dimensions, the dimensionless number is expressed as $\frac{T_0}{T}\frac{\nabla T}{T}\left(1+\frac{\nabla T}{T}\right)^{-1}$.

Expression for non-dimensional entropy generation term (or irreversibility) for one dimensional convective heat transfer is given below (Bejan 1978).

$$\frac{d\dot{I}}{q'dx} = \frac{d\dot{S}}{dx}\frac{T}{q'} = \frac{\dot{m}}{\rho q'}\left(-\frac{dP}{dx}\right) + \frac{\Delta T}{T}\left(1 + \frac{\Delta T}{T}\right)^{-1}$$

Bejan (1978) has split the non-dimensional irreversibility term into two parts: the loss of kinetic energy of fluid due to fluid friction (viscous effects), $\frac{\dot{m}}{\rho}\left(-\frac{dP}{dx}\right)$ is equivalent to the loss of energy during work transfer process and is captured by the W_{loss} term and the second part $q'\frac{\Delta T}{T}\left(1 + \frac{\Delta T}{T}\right)^{-1}$ corresponds to the thermal irreversibility.

Shaw and Skiepko (2004) used a dimensionless entropy generation term. The generalised expression for the dimensionless entropy generation term in one dimension was given as $S^* = \frac{S_{gen}T_0}{q}$. Wenterodt and Herwig (2004) introduced a new term 'entropic potential', $\frac{E}{T_0}$, of energy E to assess thermal irreversibility during energy transfer process. The ratio of the entropy generation term and the entropic potential of energy was defined as an energy devaluation number: $\frac{S_{gen}T_0}{q}$. For a fully developed pipe flow the expression for the energy devaluation number is given as $\frac{\Delta T\,T_0}{T^2}$. Herwig (2016) concludes that the temperature level on which the heat transfer occurs is important and the Nusselt number does not include this information. The energy devaluation number quantifies the quality of heat transfer between zero and one as fraction of consumption of the entropic potential. However, Herwig's newly proposed energy devaluation number has a striking similarity with the previously defined dimensionless entropy generation number when $\Delta T \ll T$.

$$\frac{S_{gen}\,T}{q} = \frac{\Delta T}{T}$$

$$\frac{S_{gen}\,T_0}{q} = \frac{S_{gen}\,T}{q}\,\frac{T_0}{T} = \frac{\Delta T}{T}\,\frac{T_0}{T} = \frac{\Delta T\,T_0}{T^2}$$

If $\Delta T \ll T$ condition is satisfied, then the dimensionless entropy generation term is given by:

$$S^* = \frac{S_{gen}T_0}{q} = \frac{\delta CW_{net}}{q}\,\frac{T_0}{T} = \frac{T_0}{T}\,\frac{\Delta T}{T}$$

$\Delta T \ll T$ condition is not satisfied then the dimensionless entropy generation term is given by:

$$S^* = \frac{S_{gen}T_0}{q} = \frac{\delta CW_{net}}{q}\,\frac{T_0}{T} = \left(\frac{T_0}{T}\right)^2 \frac{\Delta T}{T}\left(1 + \frac{\Delta T}{T}\right)^{-1}$$

If $\Delta T \ll T$ then $1 + \frac{\Delta T}{T} \approx 1$. It is shown below that the thermal irreversibility term $q'\frac{\Delta T}{T}$ is equal to $CW_{net.}$

$$\delta CW_{net} = \delta Q\left(1 - \frac{T_0}{T + \Delta T}\right) - \delta Q\left(1 - \frac{T_0}{T}\right)$$

$$= \delta Q\left(\left(\frac{T - T_0 + \Delta T}{T}\right) - \left(\frac{(T - T_0)}{T}\right)\right)$$

$$= \delta Q\,\frac{\Delta T}{T}$$

δQ transferred over length Δx and time dt represents the heat flux and represents the quantity of heat transfer. The quality of heat transfer is given by the dimensionless ratio $\Delta T/T$ where ΔT is the temperature gradient in x direction. Therefore, for a three dimensional heat conduction problem, the local value CW_{net}, the entropy generation term S_{gen} and the entransy dissipation term Z_{diss} is:

$$CW_{net} = \boldsymbol{q}\cdot\frac{\boldsymbol{\nabla T}}{T} \tag{13}$$

$$S_{gen} = CW_{net}/T = \boldsymbol{q}\cdot\frac{\boldsymbol{\nabla T}}{T^2}$$

$$Z_{diss} = CW_{net} * T = \boldsymbol{q}\cdot\boldsymbol{\nabla T}$$

Equation 13 highlights that the same temperature gradient on a higher temperature level contributes less to the loss of net Carnot work, or the thermal irreversibility, as compared to a lower temperature level. It is suggested that researchers using the entransy dissipation principle for minimising thermal irreversibility, instead of the commonly used entropy generation principle, understand the limitation posed this subtle difference.

The minimization of thermal irreversibility corresponds to minimising the δCW_{net} value. Ideally the dot product of heat flux and the ratio $\frac{\Delta T}{T}$ i.e. the term $\frac{k(\Delta T)^2}{T}$ needs to be minimised. Therefore the term $\frac{1}{T}$ is not added blindly into the irreversibility measure. It is shown that the dimensionless ratio $\frac{\Delta T}{T}$ is an integral part of the thermal irreversibility measure irrespective of the objective of the heat transfer whether it is for heat-work conversion, or for achieving heating or cooling effect. The entransy minimisation term loses a link with the temperature level T on which the heat flux $\boldsymbol{q}$ occurs. This affects its ability to account for the quality of heat transfer.

6. A numerical simulation example for an unsteady process with heat generation and natural convection within an adiabatic control volume.

The objective of this numerical simulation is to determine entropy change value, $\Delta S_{ideal,sim}$, under ideal conditions (Equation 17) and compare with a numerically calculated value for the entropy change, ΔS_{ideal}, using Equation 14. The local entropy generation values are calculated in order to estimate the entropy change value under real conditions, ΔS_{real} (Equation 19).

A simplified SIMPLEC model with gravity and energy function is used an ANSYS Fluent simulation. The transient heat transfer with natural convection is modelled using incompressible ideal air. Assume that an adiabatic 5m cube is filled with air at 101 kPa and 300 K. Using ideal gas law, the density of air is 1.1731 kg/m³. Thermal conductivity, k and Dynamic Viscosity, µ values for air are taken as 26.38*10⁻³ W/ m K and 18.45*10⁻⁶ N s/m². The specific heat value at constant pressure, C_P is 1.005 kJ / kg K.

As shown in Figure 7 (a), a 2kW electric resistance heater with a square cross section of 0.5m side and 1 m length is placed in the center of the cube at the bottom surface. The volume of the heater is volume 0.25m³. The surface area of the heater is calculated as 2.25 m² i.e. (4*(1*0.5)+(0.5*0.5) = 2.25 m²). To simulate a heater in a room, a 3D model of a 5m³ was created with a Boolean subtract of volume 0.25m³. The mass of air in the control volume is 146.34 kg i.e. (1.1731 kg/m³ *174.75 m³ = 146.34 kg). The heat flux in the room is calculated as 2000/2.25 = 888.89 W/m². 1900 kJ of heat was added in the control volume over 950 seconds in 95 steps with each time step size of 10 seconds. Thus the heat added at each of the 95 time steps through the heater surface is 20kJ. The corresponding temperature increase is 12.92K i.e. (1900/(146.34*1.005) = 12.92). The expected final temperature of air is 312.92K.

As explained in Section 3.2, the increase in the entropy under ideal conditions, ΔS_{ideal}, due to δW_{loss}, or δQ_{gain}, is calculated by integrating the (δQ_{gain} / T_{mass}) term from an initial ($T_{initial}$) to a final (T_{final}) condition. It contributed to the entropy generation term. The heat gain, δQ_{gain}, appears within the control volume under ideal conditions. In other words, it is assumed to be uniformly generated across the control volume. With uniform temperature conditions, there were no spatial temperature gradients and velocity of the fluid within the control volume was zero. There is no heat transfer across finite temperature difference within the control volume. Therefore, the net Carnot work output opportunity, δCW_{net}, during the heat gain process, or the thermal irreversibility, is zero. It is also assumed that there is no unaccounted heat dissipation, δQ_{loss}, to immediate surrounding. Note that the value of $\dot{Q}_{flux}$ in the following equation is 2kW.

$$\Delta S_{ideal} = \int \frac{\dot{Q}_{flux}}{T} \, dt = mC_P \ln\left(\frac{T_{final}}{T_{initial}}\right) = 146.34 * 1005 * \ln\left(\frac{312.92}{300}\right) = 6201.3 \, J/K \qquad (14)$$

Figure 7 (a) and (b) shows the model and the mesh applied. A general mesh size of 0.25 m was applied to the model after conducting the mesh independency study shown in Figures 7 (c) and (d). As heat transfer occurred around the Boolean subtract, a mesh refinement was applied in this section. Once a mesh independency study was conducted, this refinement was 0.03m.
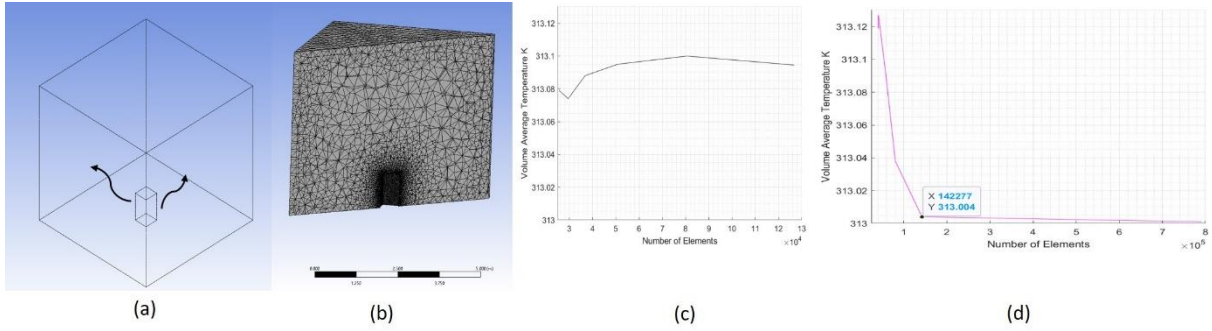
Figure 7. (a) Control volume showing 5m adiabatic cube with a heater shown in the bottom centre. (b) Mesh shown at the diagonal cross section refined after mesh sensitivity study as shown in (c) and (d).

Whilst the simulation ran, volume averaged temperature, $\bar{T}$ in K and entropy, $\bar{\dot{S}}$ in W/ m³ K were calculated as follows.

$$\bar{T} = \frac{1}{V} \int T_{local} dV = \frac{1}{\sum V_{local}} \sum T_{local} V_{local} \tag{15}$$

$$\bar{\dot{S}} = \frac{1}{V} \int \dot{S}_{local} dV = \frac{1}{\sum V_{local}} \sum \dot{S}_{local} V_{local} \tag{16}$$

Where $T_{local}, V_{local}, \dot{S}_{local}$ are nodal temperature, volume and entropy rate values.

The volume average temperature increase from the simulation is 13.08K and the volume averaged entropy change, $\Delta S_{ideal,sim}$, is calculated using Equation 16 as follows:

$$\Delta S_{ideal,sim} = \bar{\dot{S}}_{final} - \bar{\dot{S}}_{initial} = 42.5 \text{ J/Kg K} = 42.5 * 146.34 = 6219.45 \text{ J/K}. \tag{17}$$

The simulation error is less than 1.25% for temperature prediction and 0.3% for entropy change estimates. The temperature contours at the final timestep (950 seconds) at five planes at -2, -1, 0, 1 and 2 m location as shown in Figure 8 (a) are illustrated in Figure 8 (b-f). The corresponding velocity vectors at plane 0m are shown in Figure 9. It can be observed that the velocity of the air accelerates around the heater and follows the path of the temperature funnel shown.
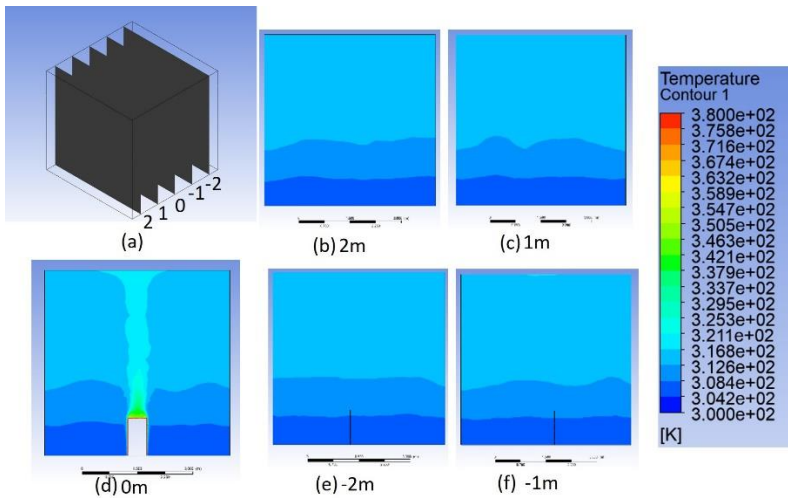

Figure 8. (a) Cut sections at five locations from the centre 0m and at 1 and 2 m at each side. (b-f) Temperature distribution from the ANSYS model at 950 seconds.
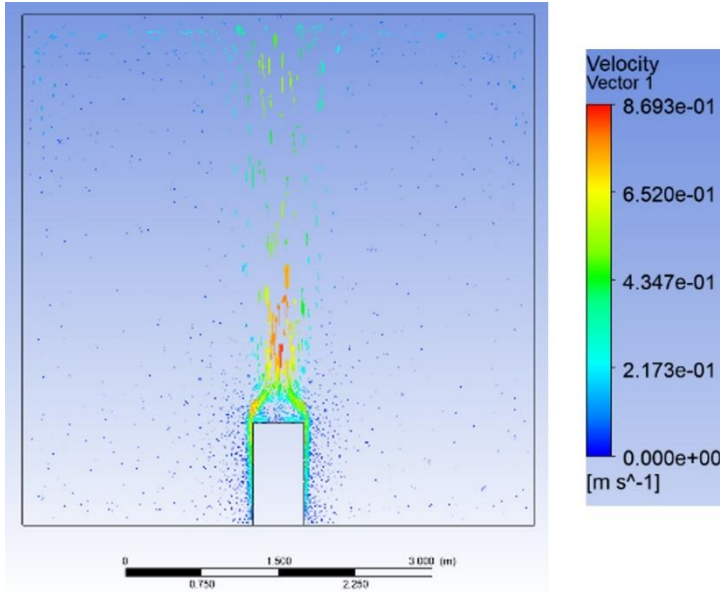
Figure 9. Velocity vectors for air due to natural convection from the ANSYS model at 950 seconds.

The close inspection of results around the heating section showed (partly shown in Figure 8, 0m plane) overheating of air to temperatures up to 600K. This is unrealistic although not surprising due to the simplistic model chosen in the ANSYS simulation. A selection of 2500 nodes was made around the heating section to estimate the volume averaged boundary temperature, $\bar{T}_b$, at the heating section. After 200 seconds, ie. 20 time steps, its value approximately remained constant at 522K. For the first 200 seconds the $\bar{T}_b$ value is approximated as 300K.

$$\bar{T}_b = \frac{1}{\sum V_{b,local}} \sum T_{local} V_{b,local} \tag{18}$$

As derived in Equation 13, for a heat conduction problem, the local entropy generation term represents a temperature standardised value of Carnot (reversible) work opportunity. For the ANSYS simulation illustrated in Figure 7 (a), the input heat flux, $\dot{Q}_{flux}$, through the heating section is 2kW. As discussed in Section 3.3, the entropy change value is same for real, ΔS_{real}, and ideal, $\Delta S_{ideal,sim}$, conditions.

$$\Delta S_{ideal,sim} = \Delta S_{real} = \sum_{i=1}^{n} \left\{ \left[\frac{\dot{Q}_{flux}}{\bar{T}_b} + V\bar{\dot{S}}_{gen} + V\bar{\dot{S}}_{gen,unaccounted} \right] \Delta t \right\}_i \tag{19}$$

where,

N = number of timesteps and t = duration of timestep,

$$\bar{\dot{S}}_{gen} V = \bar{\dot{S}}_{gen} \sum V_{local} = \sum \dot{S}_{gen,local} V_{local}$$

$$\dot{S}_{gen,local} = \dot{S}_{cond} + \dot{S}_{conv}$$

$$\dot{S}_{cond} = \frac{1}{T^2} q \cdot \nabla T$$

$$\dot{S}_{cond} = \frac{k}{T^2}\left\{\left(\frac{\partial T}{\partial x}\right)^2 + \left(\frac{\partial T}{\partial y}\right)^2 + \left(\frac{\partial T}{\partial z}\right)^2\right\}$$

$$\dot{S}_{conv} = \frac{\mu}{T}\varphi$$

$$\varphi = 2\left\{\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial y}\right)^2 + \left(\frac{\partial w}{\partial z}\right)^2\right\} + \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)^2$$

The volume averaged entropy generation, caused by viscous dissipation, $V\bar{\dot{S}}_{conv}$, is negligible in value i.e. $44*10^{-9}$ W/m³K (0.000289 J/K). The time integrated entropy generation value, $V\bar{\dot{S}}_{gen}$, is calculated as 144.7 J/K.

$$\Delta S_{ideal,sim} = \Delta S_{real} = 6219.45 \, J/K$$

$$\Delta S_{real} = \sum_{i=1}^{20}\left[\frac{\dot{Q}_{flux}\,\Delta t}{\bar{T}_b}\right]_i + \sum_{i=21}^{95}\left[\frac{\dot{Q}_{flux}\,\Delta t}{\bar{T}_b}\right]_i + \sum_{i=1}^{95}\left[V\bar{\dot{S}}_{gen}\,\Delta t\right]_i + \sum_{i=1}^{95}\left[V\bar{\dot{S}}_{gen,unaccounted}\Delta t\right]_i$$

$$6219.45 \, J/K = \frac{20*2000*10}{300} + \frac{75*2000*10}{522} + 144.7 + S_{gen,unaccounted}$$

$$6219.45 \, J/K = 1333.33 + 2873.56 + 144.7 + S_{gen,unaccounted}$$

$$S_{gen,unaccounted} = 1867.86 \, J/K$$

The $S_{gen,unaccounted}$ value has resulted from almost certainly due to the temperature spike around the heating section and the approximation used in calculating the $\int\frac{\dot{Q}_{flux}}{T}\,dt$ term. The average $\bar{T}_{b,avg}$ value is back calculated from $V\bar{\dot{S}}_{gen}$ and ΔS_{real} values as follows:

$$\bar{T}_{b,avg} = \frac{20*2000*10*95}{6219.45 + 144.7} = 312.8 \, K$$

This value is close to the estimated volume averaged final temperature of air in the control volume. For ideal conditions, as there is no thermal irreversibility, this estimate should approximate to the average of final and initial temperatures. The calculation of $\bar{T}_{b,avg}$ as 306.4 K gives confidence in the reliability of the methodology used.

$$\bar{T}_{b,avg} = \frac{20*2000*10*95}{6201.3} = 306.4 \, K$$

Using Equation 13, the loss of Carnot (reversible) work opportunity, CW_{net}, resulting from heat transfer across finite temperature difference within the adiabatic control volume is calculated as follows:

$$CW_{net} = T_{avg}\sum_{i=1}^{95}\left[V\bar{\dot{S}}_{gen}\,\Delta t\right]_i = \frac{300+313.08}{2} * 144.7 = 44.36 \, kJ$$

It should also be noted that the proposed understanding of thermal irreversibility does NOT alter various mathematical formulations proposed by Bejan, and many other researchers, on entropy generation minimization techniques including topics such as unsteady flow and convective heat transfer. However, the proposed insights should explain why it is impossible for thermal (or heat transfer) irreversibility value to approach zero even when heat is transferred across a finite temperature difference without any energy dissipation. The thermal irreversibility represents the loss of opportunity to do useful work by exchanging heat with surroundings during the heat transfer process across a finite

temperature difference. This insight explains one practical way of minimising thermal irreversibility that is the reduction of the magnitude of heat transfer across a finite temperature difference using one or more methods e.g. employing regeneration, or heat storage, techniques at elevated temperatures.

7. Conclusion

It is shown that the ambient temperature, the temperature of mass and the temperature of external bodies with which the mass has exchanged heat are not added blindly into the irreversibility measure and is based on the definition of thermal irreversibility. When heat is transferred across a finite temperature difference, the opportunity to extract useful work is lost. This loss, estimated by thermal irreversibility calculations, is independent of the purpose of heat transfer whether heat is transferred to heat or cool an object or achieve heat-to-work conversion. The entransy minimization term loses a link with the temperature level on which the heat flux occurs and hence, it degrades the information content of the entropy generation term S_{gen}.

The entropy of a mass at any given state is defined as the net temperature-standardised heat transfer to mass under ideal conditions measured from a datum value. This interpretation is consistent with how entropy values are calculated in Classical thermodynamics. The entropy value is assumed to be zero at a given reference/datum temperature value including the absolute zero, and the subsequent entropy change is calculated by combining the conservation of energy and the Clausius inequality expressions. It is argued that the entropy change of mass is defined as a measure of the heat transfer the mass has experienced under ideal conditions.

The commonly held view that irreversibility during heat and work transfer process has the same physical interpretation as 'dissipation of energy in terms of lost work' is challenged in this paper. The irreversibility has three parts: (i) the loss of work, W_{loss}, in a work transfer process, (ii) the dissipation of unaccounted heat, Q_{loss}, during a heat transfer process, and (iii) the missed opportunity to create the net Carnot work, CW_{net}, during heat transfer across a finite temperature difference. Its numerical value is the same as the exergy destruction term, $T_0 S_{gen}$. The loss of net Carnot work from a heat transfer process (thermal irreversibility) is visualised with an independent two-way heat exchange with its surroundings through a combined Carnot engine-heat pump that delivers the same amount of heat across a finite temperature difference, and produces a net Carnot work output. Hence, thermal irreversibility is not 'dissipation energy in terms of lost work' but represents 'a notional loss of work opportunity' or 'a missed opportunity to do useful work by exchanging heat with the surrounding'. It is also explained in this paper, how the net Carnot work output value further reduces the reversible work input estimation of an internally reversible compressor that is losing heat to its surroundings. The Gibbs and Helmholtz energy is linked to the entropy balance equation and shown to be a measure of loss of exploiting the Carnot work opportunity by exchanging heat with surrounding rather than interpreting it as a source of 'free' energy.

Once we understand how the irreversibility occurs at every stage of a heat and work transfer process, the thermodynamics insights gained have potential to lead to the development of innovative design solutions.

Conflict of Interests

The author confirms that the views presented in the manuscript are his own personal and impartial views. These are not influenced by any form of financial incentives and nationalism. He does not have bias against, or towards, any thermodynamic concept including entransy. He has attempted to address all open and unanswered questions in the literature relating to entropy and has tried to contribute to the fundamental understanding irreversibility during heat and work transfer processes.

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